13.6

Interpreting Proton NMR Spectra

Information contained in an NMR spectrum includes:

1. number of signals
2. their intensity (as measured by area under peak)
3. splitting pattern (multiplicity)

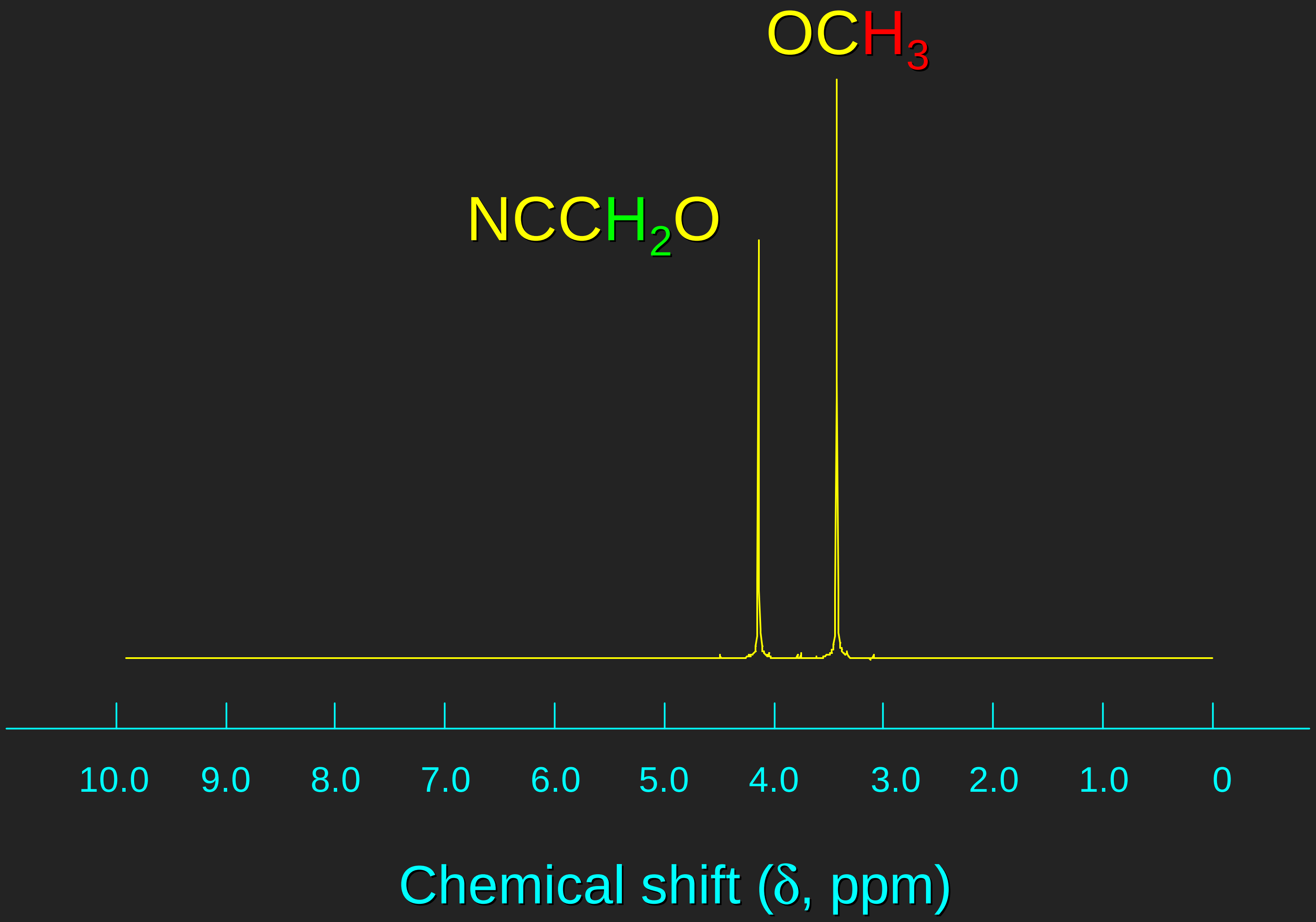
Number of Signals

protons that have different chemical shifts
are chemically nonequivalent

exist in different molecular environment

Figure 13.9 (page 497)

$N\equiv CCH_2OCH_3$

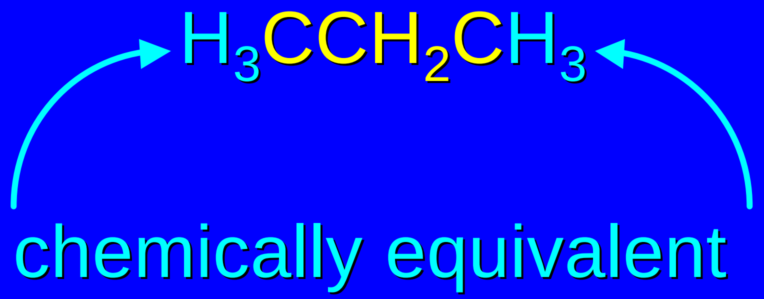


Chemically equivalent protons

are in identical environments

have same chemical shift

replacement test: replacement by some arbitrary "test group" generates same compound



$H_3CCH_2CH_3$

chemically equivalent

Chemically equivalent protons

Replacing protons at C-1 and C-3 gives same compound (1-chloropropane)

C-1 and C-3 protons are chemically equivalent and have the same chemical shift

$ClCH_2CH_2CH_3$

$CH_3CH_2CH_2Cl$

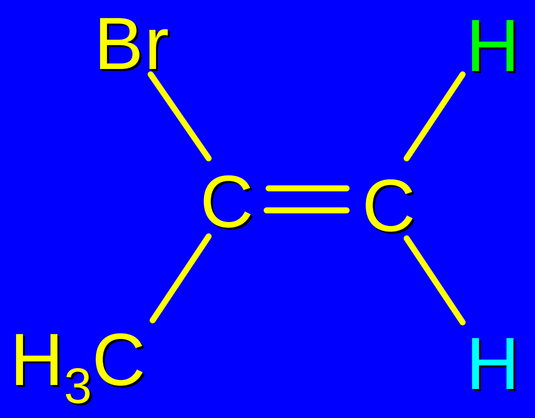
$H_3CCH_2CH_3$

chemically equivalent

Diastereotopic protons

replacement by some arbitrary test group generates diastereomers

diastereotopic protons can have different chemical shifts



δ 5.3 ppm

δ 5.5 ppm

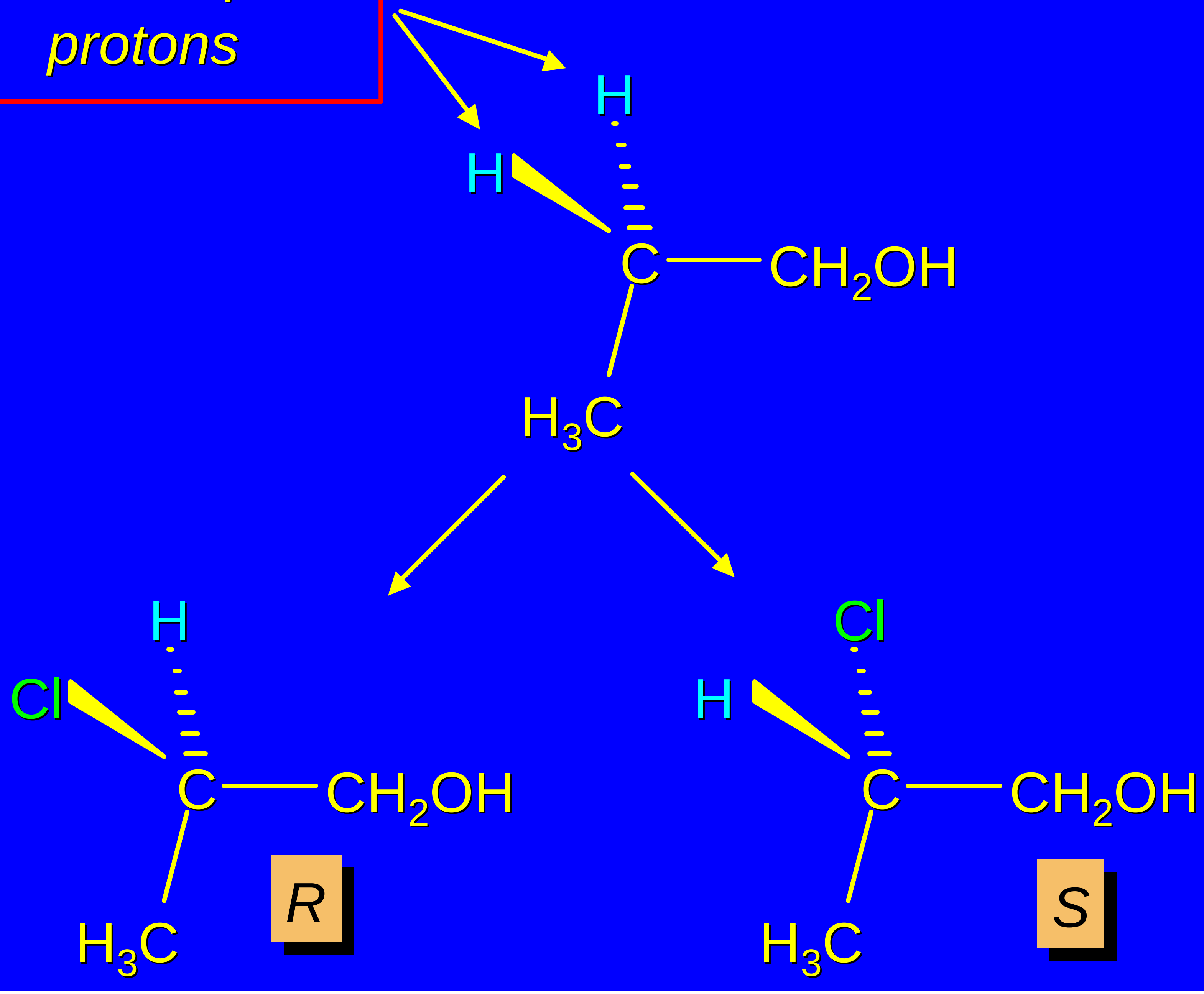
Enantiotopic protons

are in mirror-image environments

replacement by some arbitrary test group generates enantiomers

enantiotopic protons have the same chemical shift

Enantiotopic protons



13.7

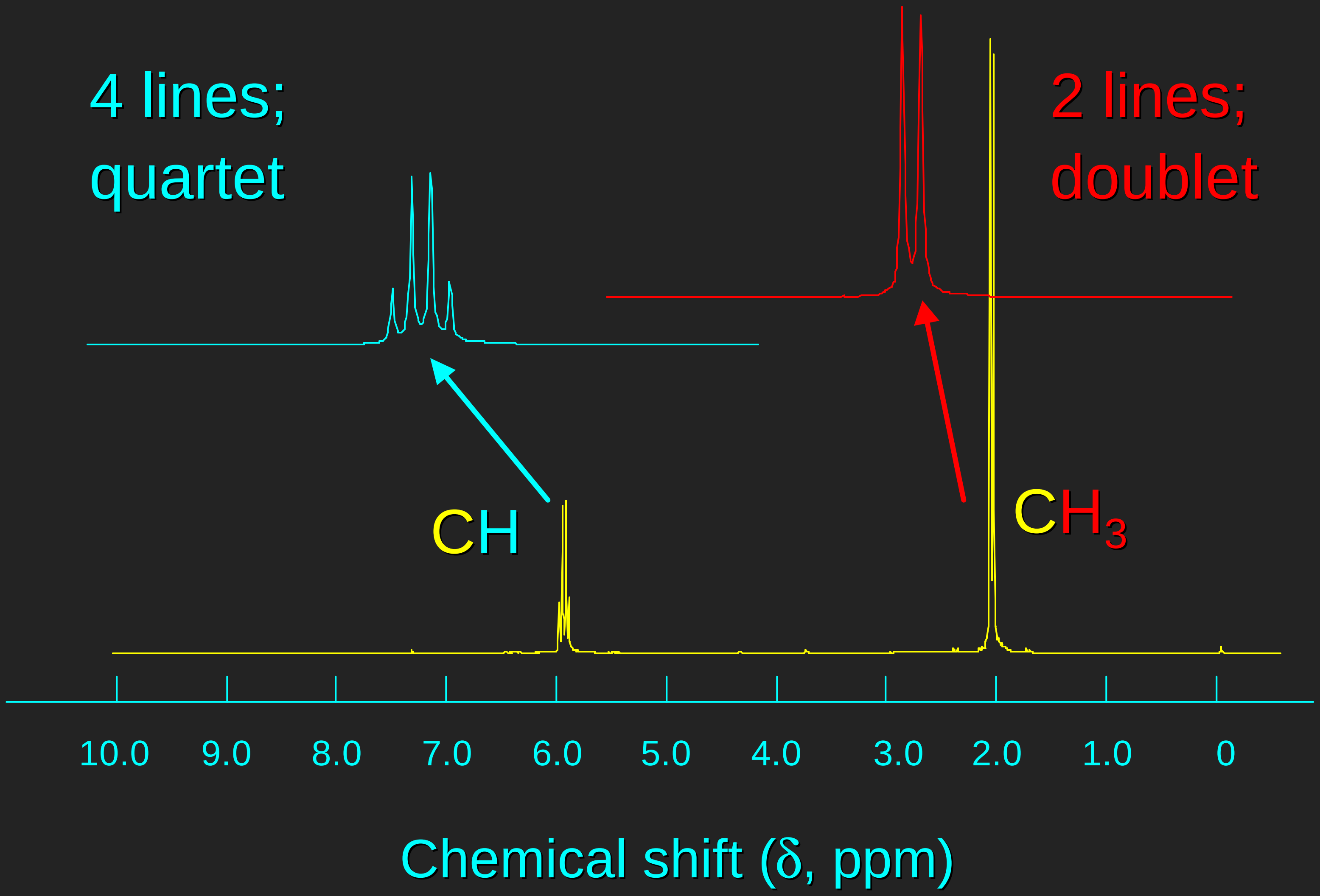
Spin-Spin Splitting in NMR Spectroscopy

not all peaks are singlets

signals can be split by coupling of nuclear spins

Figure 13.10 (page 501)

Cl_2CHCH_3



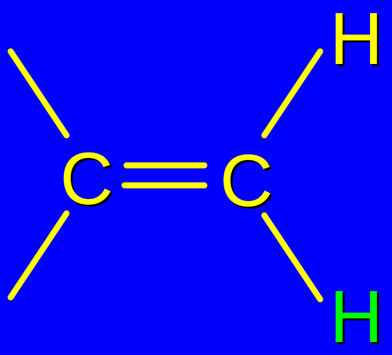
4 lines;
quartet

2 lines;
doublet

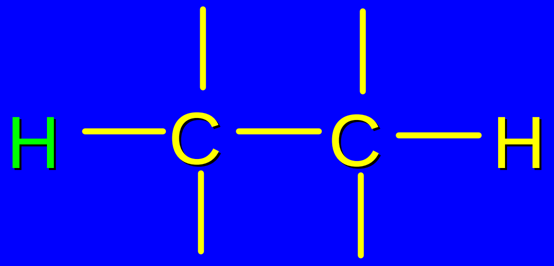
CH

CH_3

Two-bond and three-bond coupling



protons separated by
two bonds
(geminal relationship)



protons separated by
three bonds
(vicinal relationship)

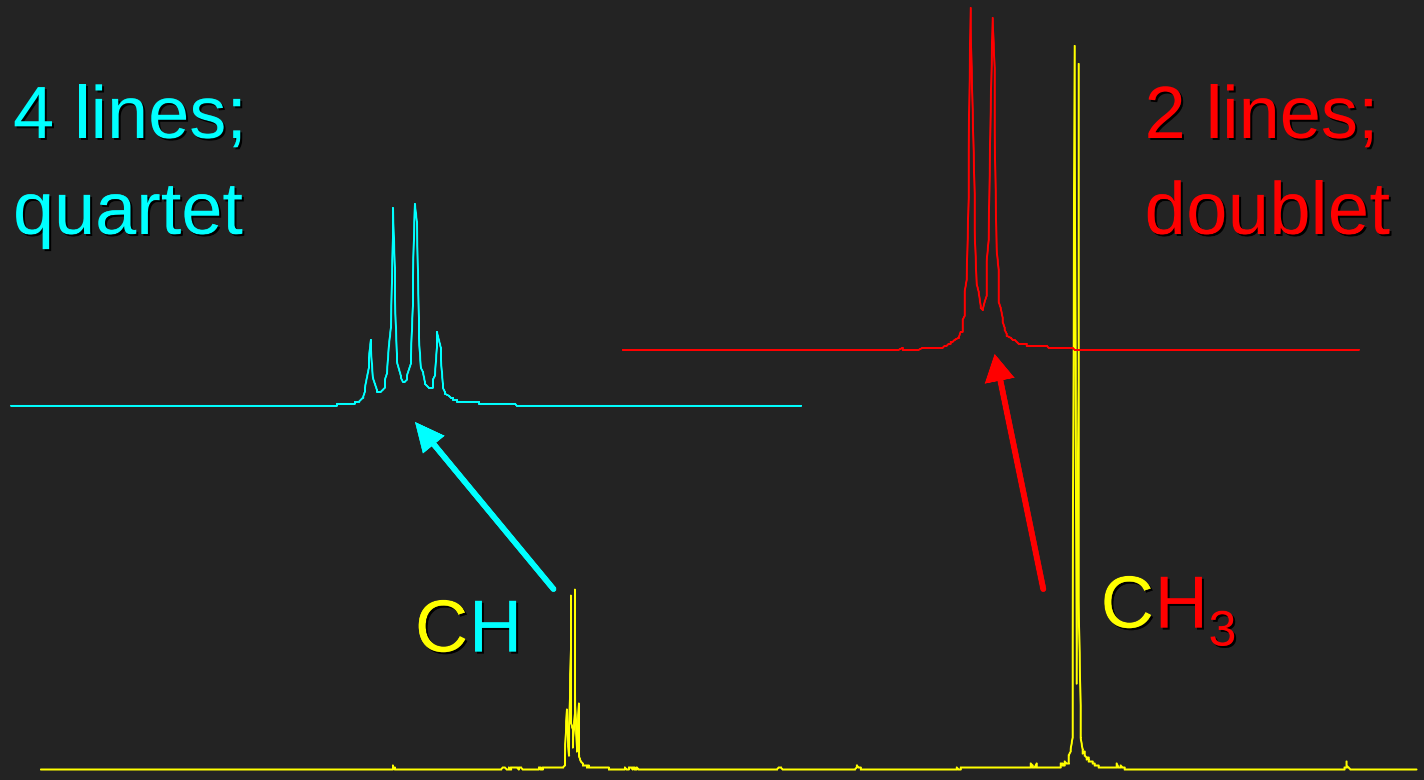
Two-bond and three-bond coupling

in order to observe splitting, protons cannot have same chemical shift

coupling constant (^2J or ^3J) is independent of field strength

Figure 13.10 (page 501)

Cl_2CHCH_3

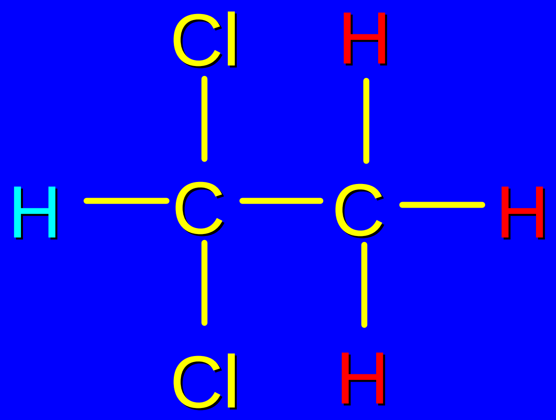


coupled protons are vicinal (three-bond coupling)

CH splits CH_3 into a doublet

CH_3 splits CH into a quartet

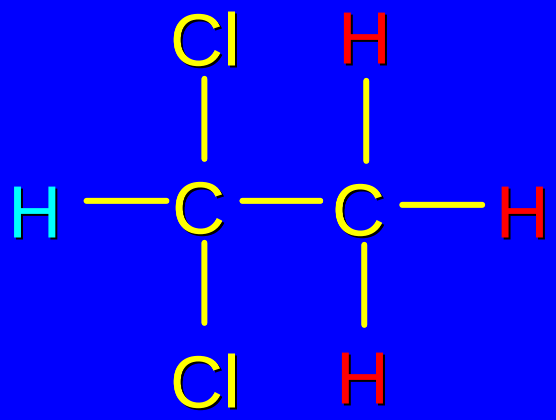
Why do the methyl protons of 1,1-dichloroethane appear as a doublet?



signal for methyl protons is split into a doublet

To explain the splitting of the protons at C-2, we first focus on the two possible spin orientations of the proton at C-1

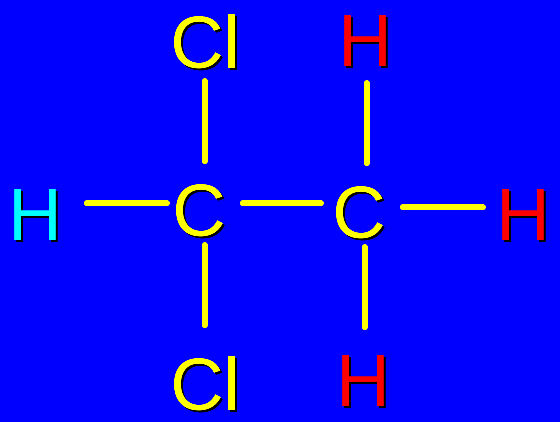
Why do the methyl protons of 1,1-dichloroethane appear as a doublet?



signal for methyl protons is split into a doublet

There are two orientations of the nuclear spin for the proton at C-1. One orientation shields the protons at C-2; the other deshields the C-2 protons.

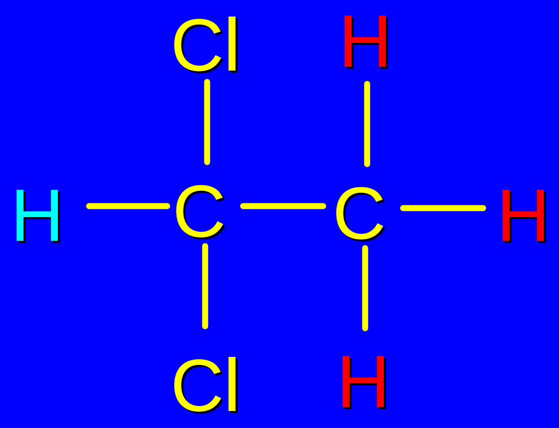
Why do the methyl protons of 1,1-dichloroethane appear as a doublet?



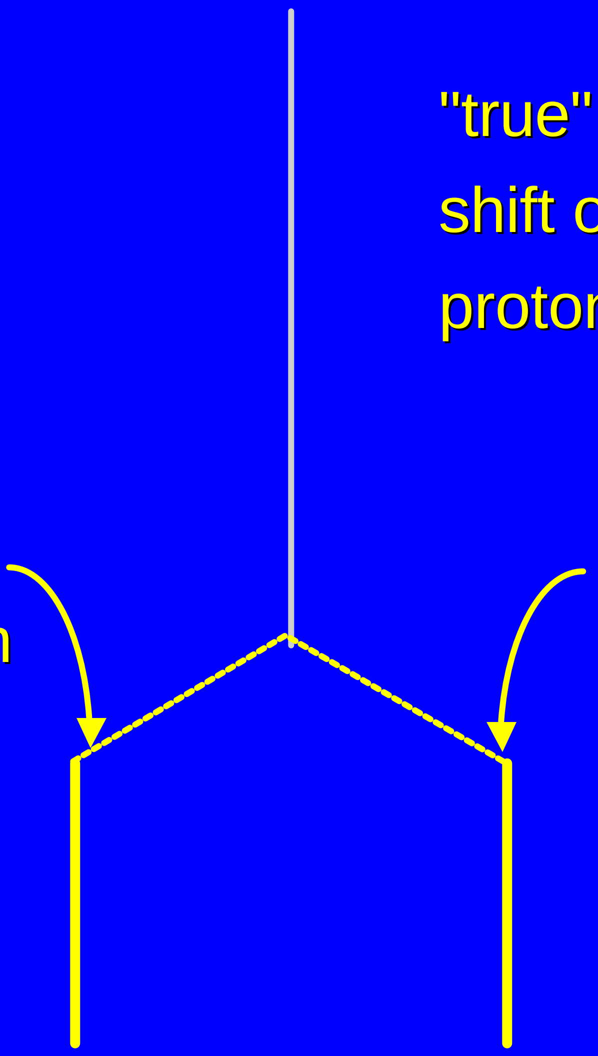
signal for methyl protons is split into a doublet

The protons at C-2 "feel" the effect of both the applied magnetic field and the local field resulting from the spin of the C-1 proton.

Why do the methyl protons of 1,1-dichloroethane appear as a doublet?



$\mathrm{HCCl_2{-}CH_3}$



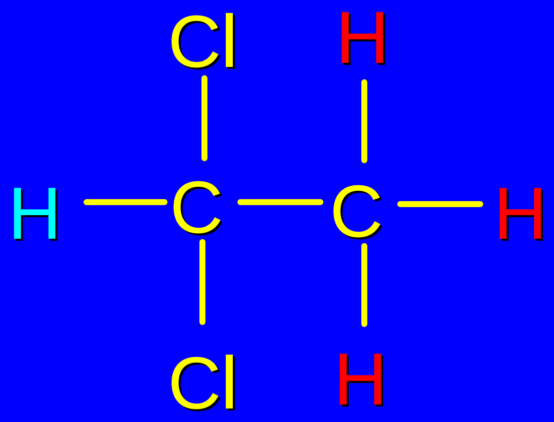
"true" chemical shift of methyl protons (no coupling)

this line corresponds to molecules in which the nuclear spin of the proton at C-1 *reinforces* the applied field

this line corresponds to molecules in which the nuclear spin of the proton at C-1 *opposes* the applied field

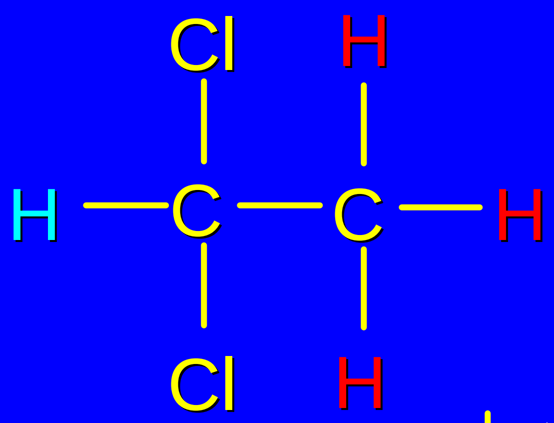
Why does the methine proton of 1,1-dichloroethane appear as a quartet?

signal for methine proton is split into a quartet



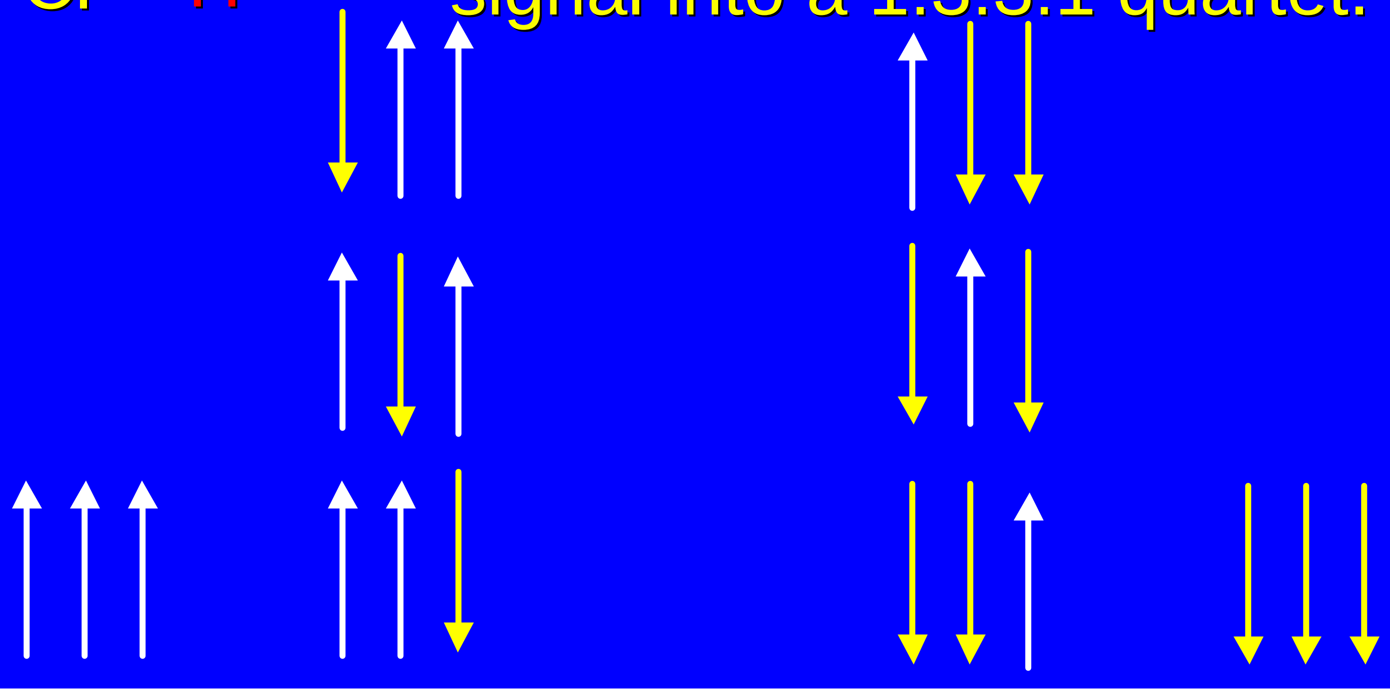
The proton at C-1 "feels" the effect of the applied magnetic field and the local fields resulting from the spin states of the three methyl protons. The possible combinations are shown on the next slide.

Why does the methine proton of 1,1-dichloroethane appear as a quartet?



There are eight combinations of nuclear spins for the three methyl protons.

These 8 combinations split the signal into a 1:3:3:1 quartet.



The splitting rule for ^{1}H NMR

For simple cases, the multiplicity of a signal for a particular proton is equal to the number of equivalent vicinal protons + 1.

Table 13.2 (page 504)

Splitting Patterns of Common Multiplets

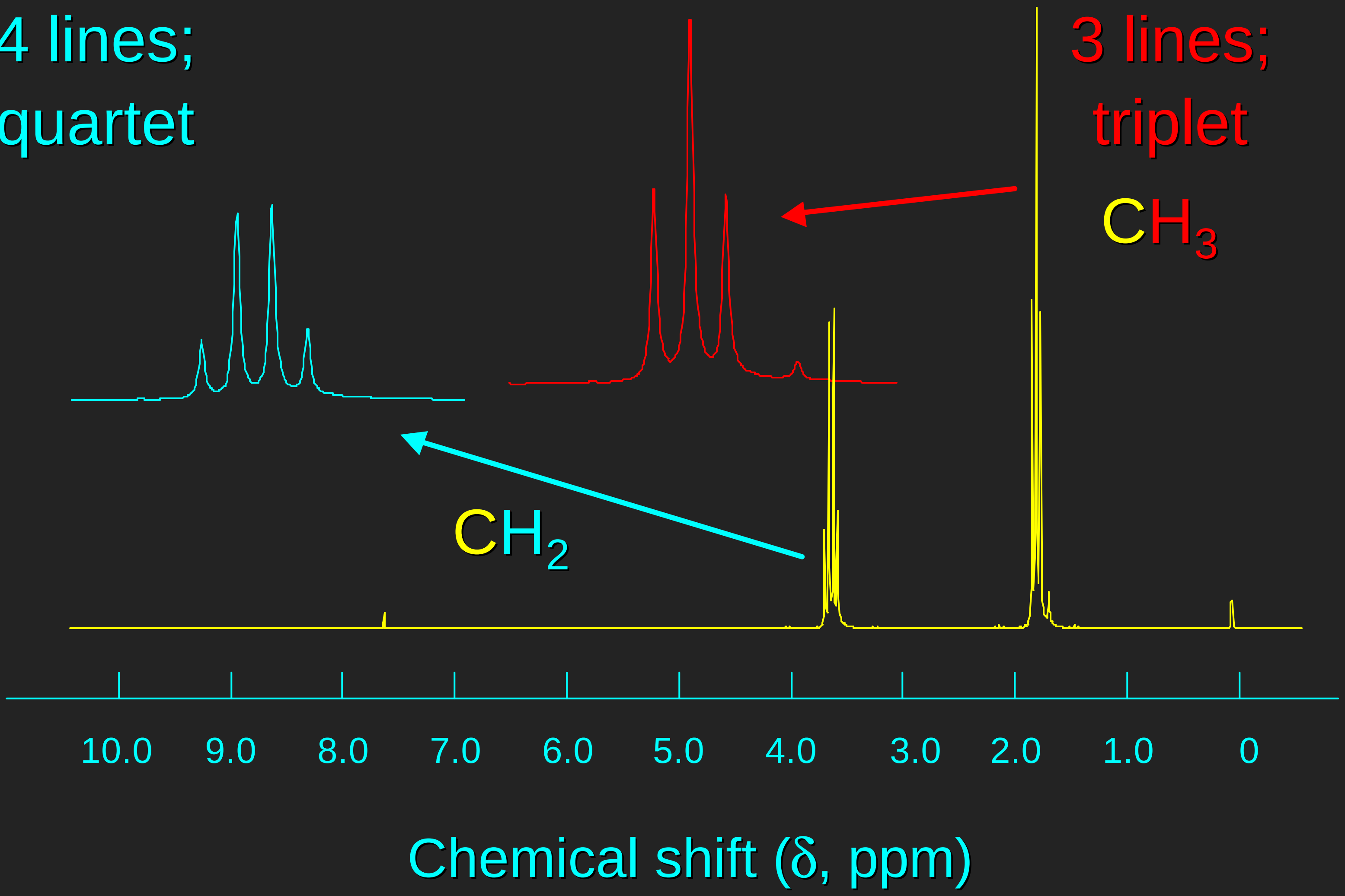
Number of equivalent protons to which H is coupled	Appearance of multiplet	Intensities of lines in multiplet
1	Doublet	1:1
2	Triplet	1:2:1
3	Quartet	1:3:3:1
4	Pentet	1:4:6:4:1
5	Sextet	1:5:10:10:5:1
6	Septet	1:6:15:20:15:6:1

13.8
Splitting Patterns:
The Ethyl Group

CH_3CH_2X is characterized by a triplet-quartet pattern (quartet at lower field than the triplet)

Figure 13.13 (page 503)

$BrCH_2CH_3$



4 lines;
quartet

CH_2

3 lines;
triplet

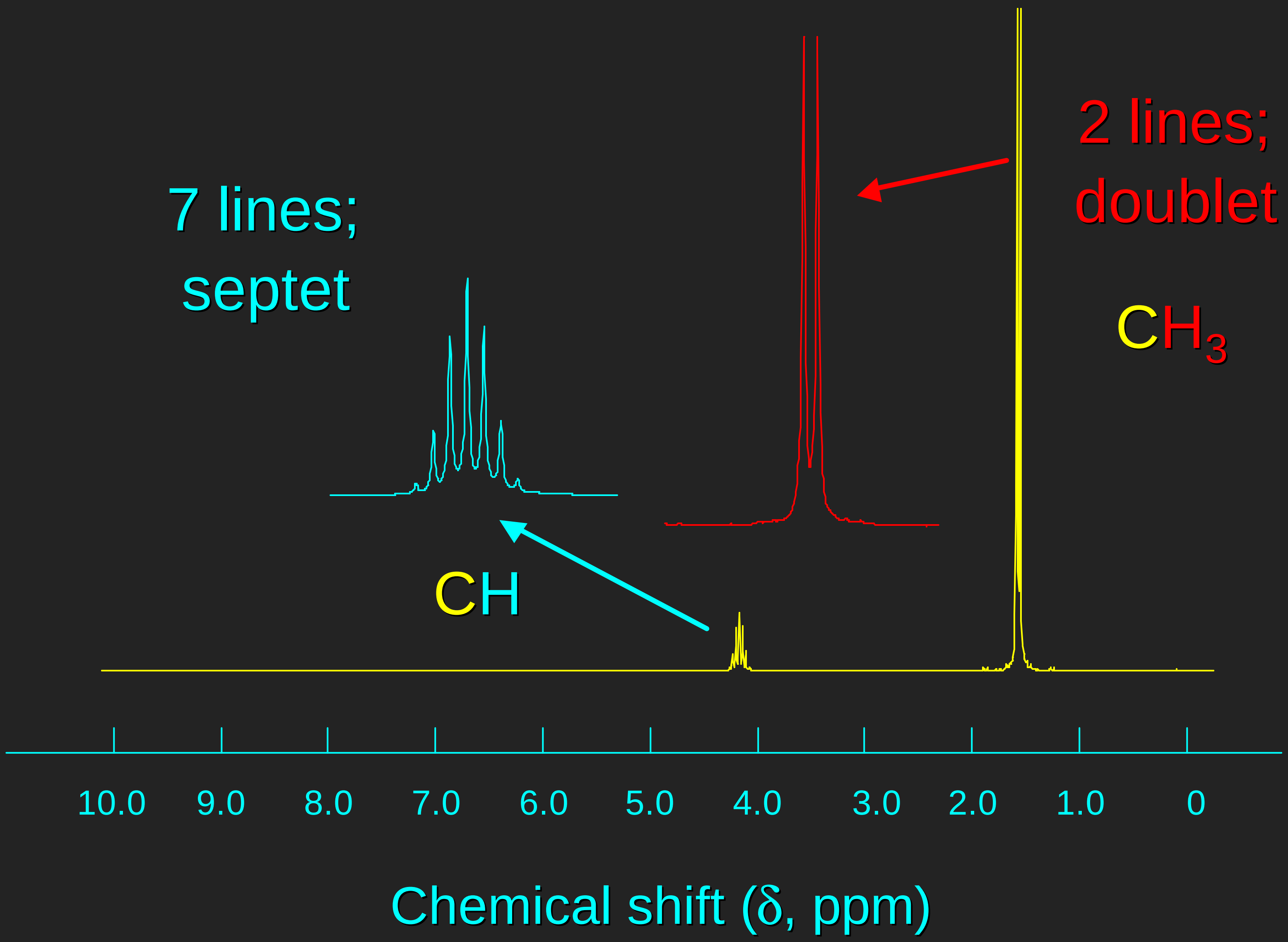
CH_3

13.9
Splitting Patterns:
The Isopropyl Group

$(CH_3)_2CHX$ is characterized by a doublet-septet pattern (septet at lower field than the doublet)

Figure 13.15 (page 505)

$BrCH(CH_3)_2$



7 lines;
septet

2 lines;
doublet

CH_3

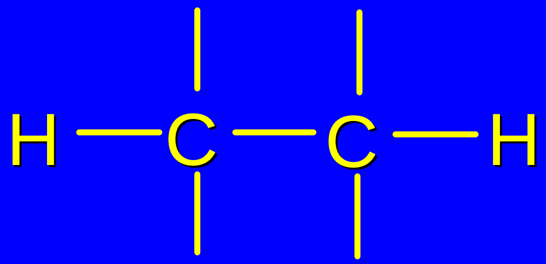
CH

13.10

Splitting Patterns: Pairs of Doublets

Splitting patterns are not always symmetrical, but lean in one direction or the other.

Pairs of Doublets

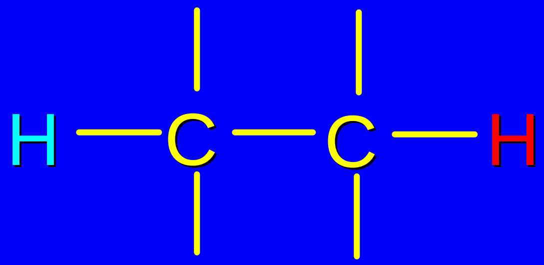


$$H-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-H$$

Consider coupling between two vicinal protons.

If the protons have different chemical shifts, each will split the signal of the other into a doublet.

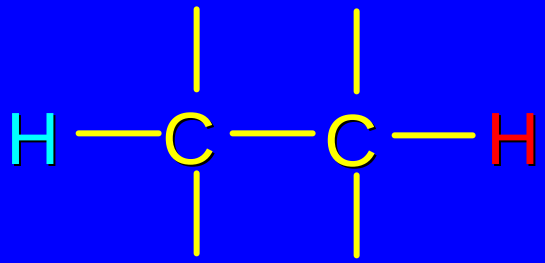
Pairs of Doublets

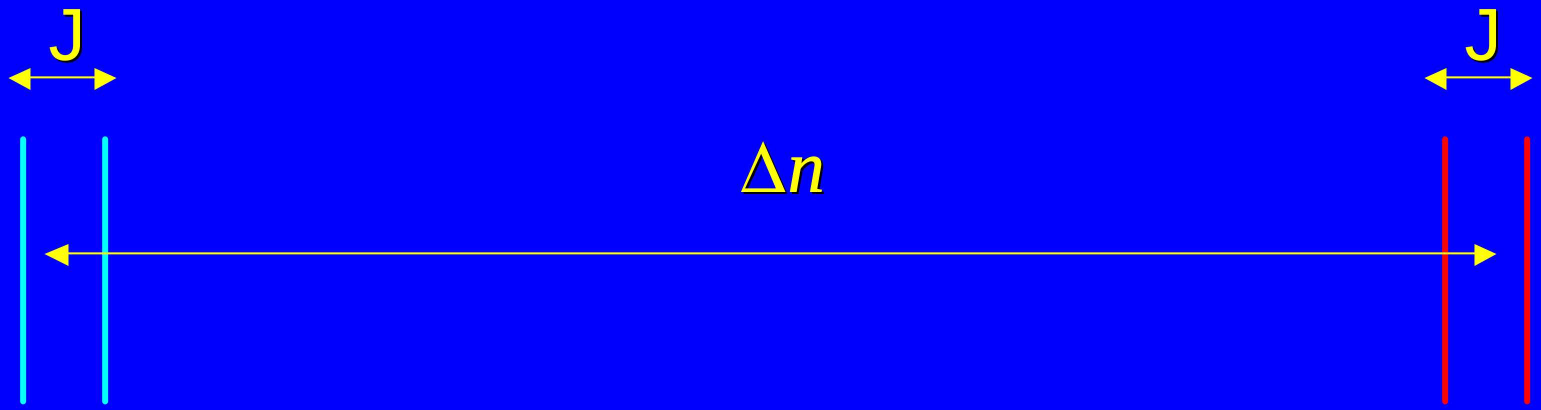


Let Δn be the difference in chemical shift in Hz between the two hydrogens.

Let J be the coupling constant between them in Hz.

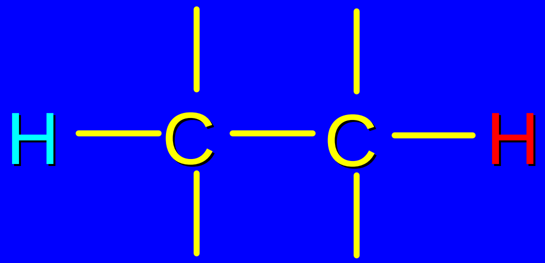
AX

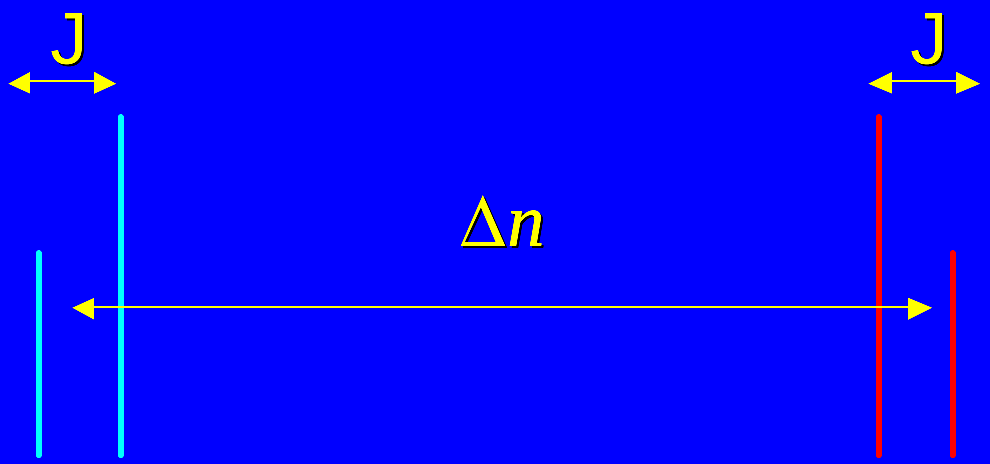




When Δ*n* is much larger than J the signal for each proton is a doublet, the doublet is symmetrical, and the spin system is called AX.

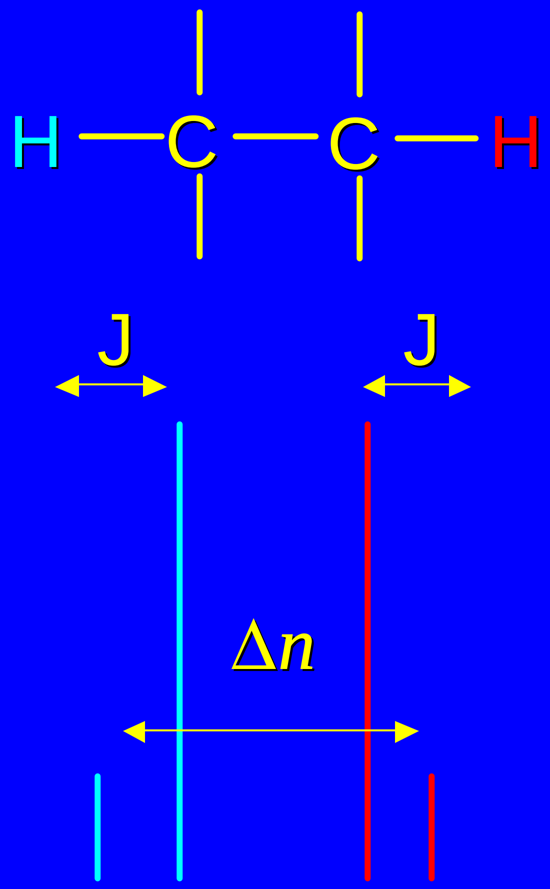
AM





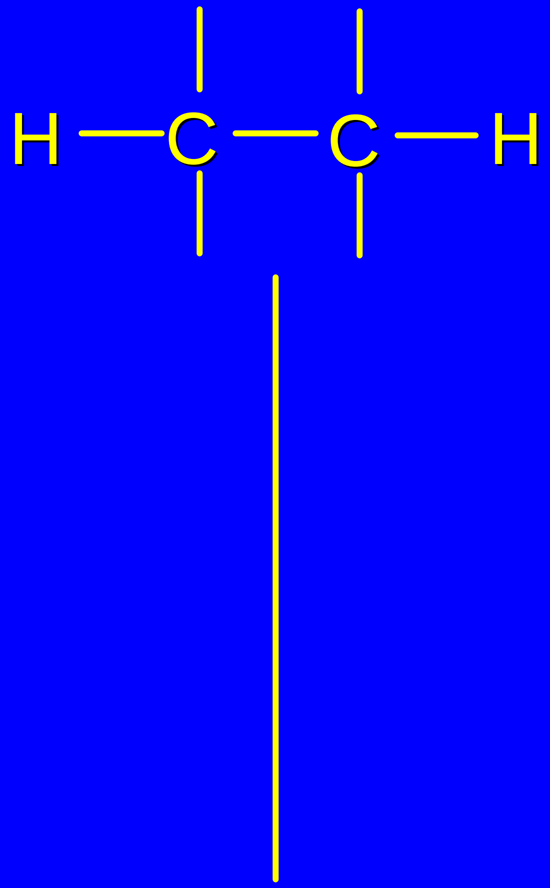
As Δn/J decreases the signal for each proton remains a doublet, but becomes skewed. The outer lines decrease while the inner lines increase, causing the doublets to "lean" toward each other.

AB



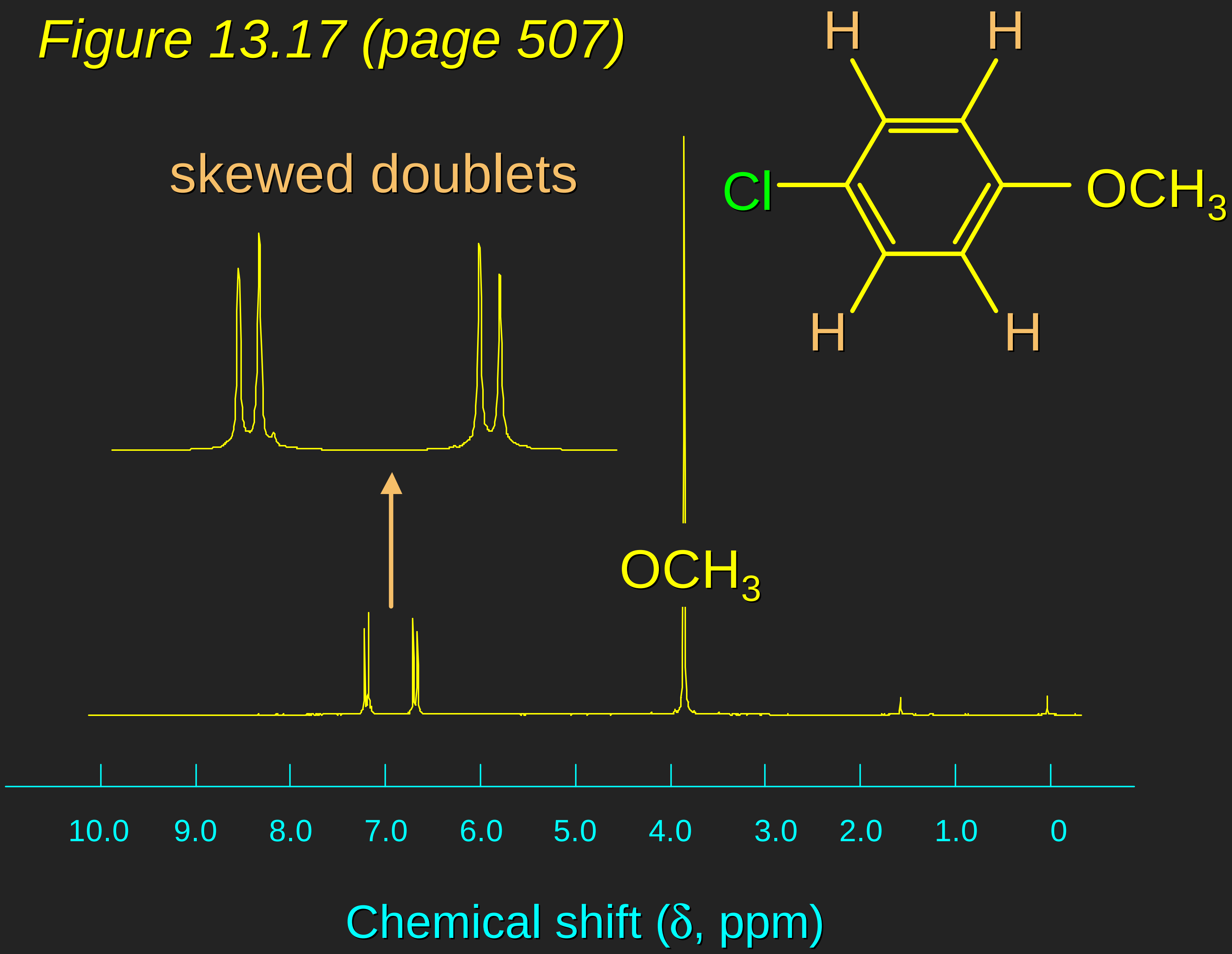
When Δn and J are similar, the spin system is called AB. Skewing is quite pronounced. It is easy to mistake an AB system of two doublets for a quartet.

A_2



When $\Delta n = 0$, the two protons have the same chemical shift and don't split each other. A single line is observed. The two doublets have collapsed to a singlet.

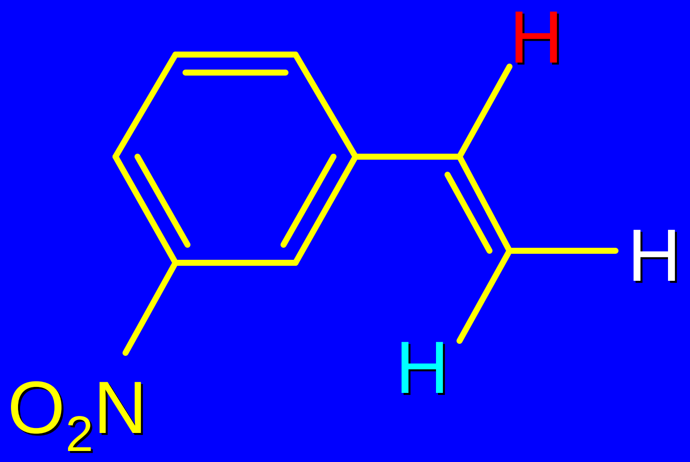
Figure 13.17 (page 507)



13.11
Complex Splitting Patterns

Multiplets of multiplets

m-Nitrostyrene

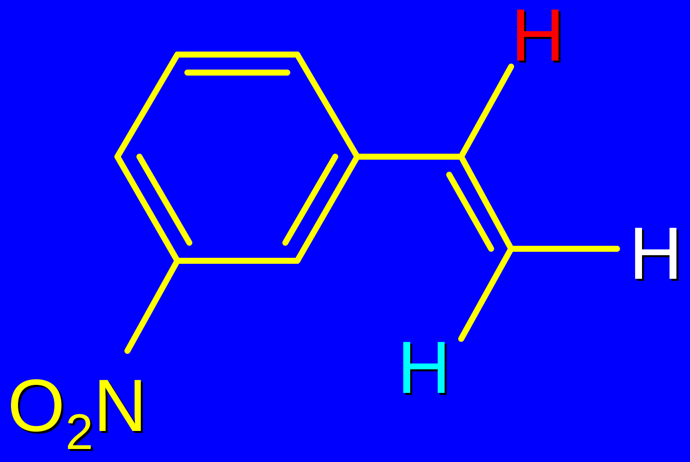


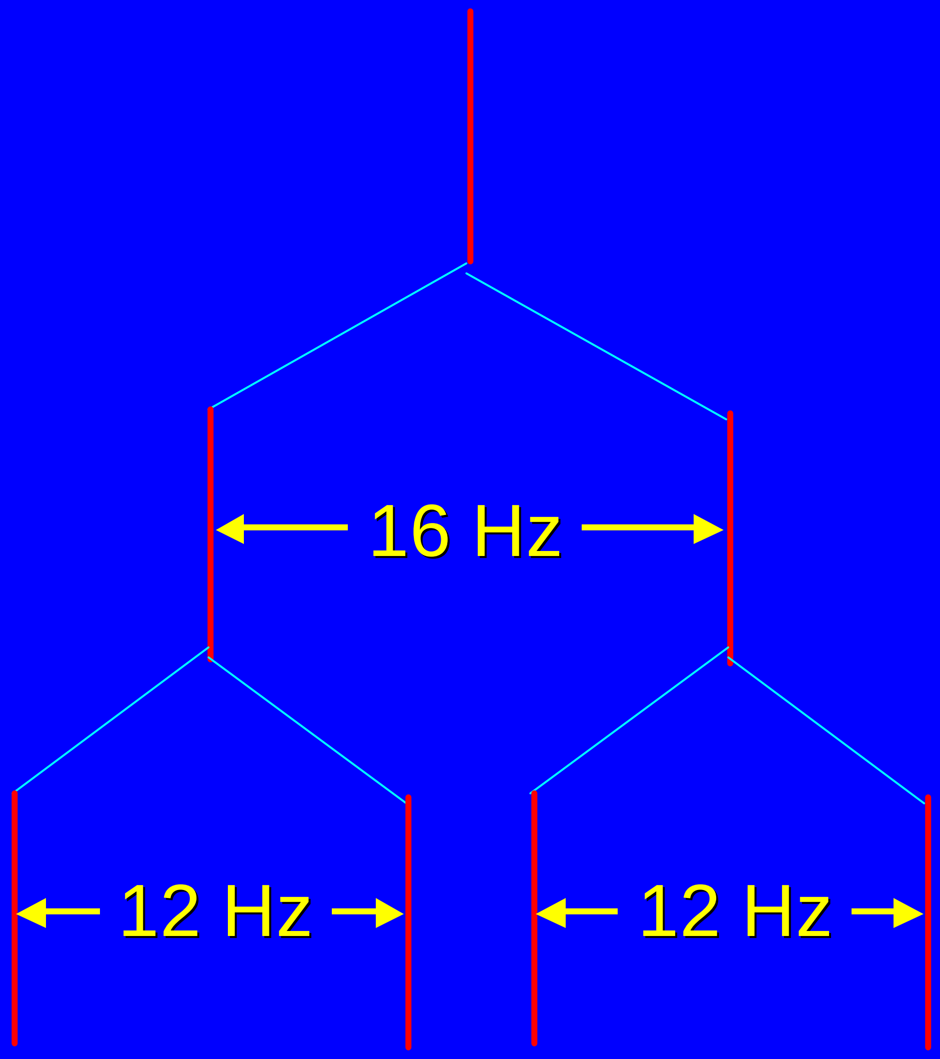
Consider the proton shown in red.

It is unequally coupled to the protons shown in blue and white.

J_{cis} = 12 Hz; J_{trans} = 16 Hz

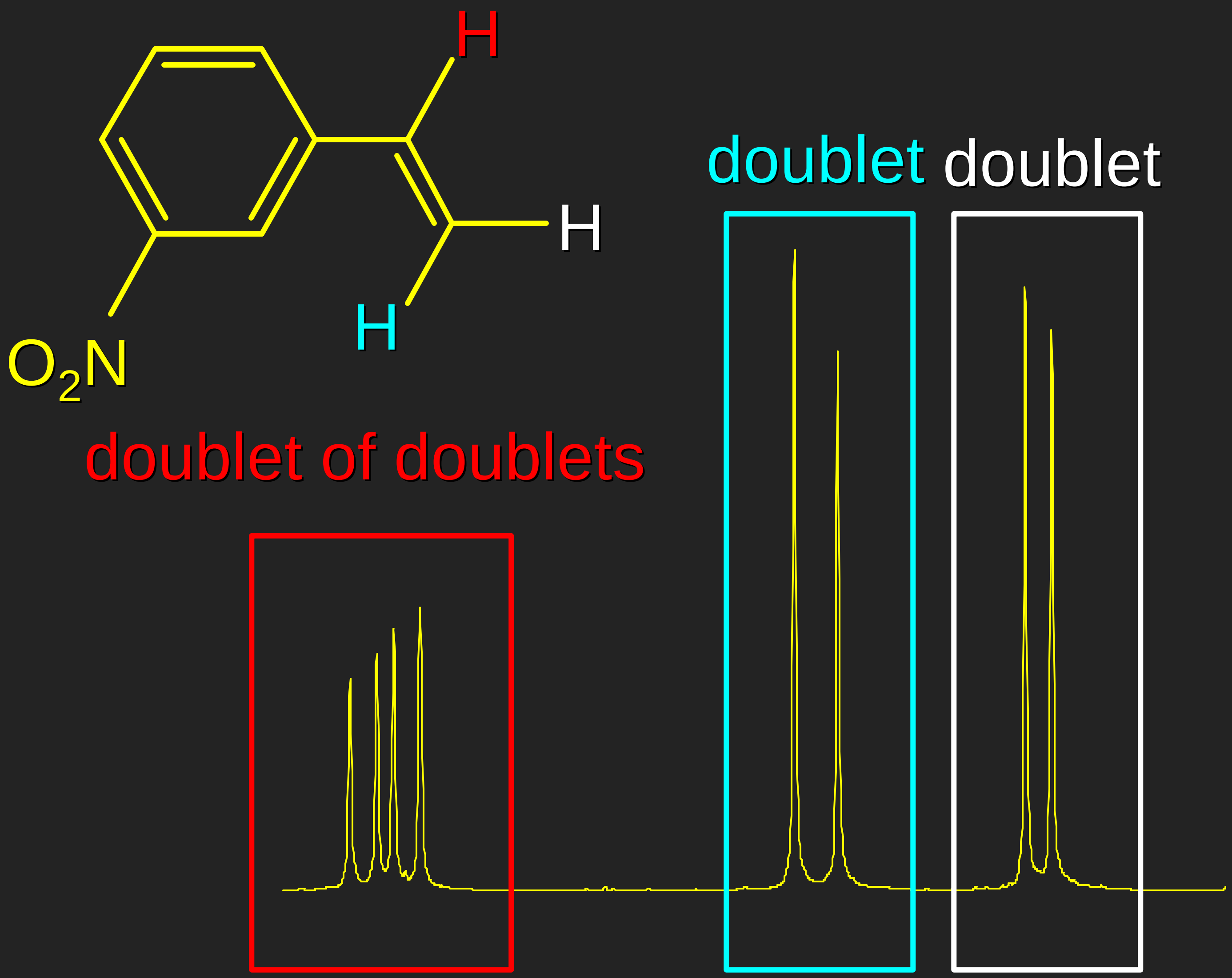
m-Nitrostyrene





The signal for the proton shown in red appears as a doublet of doublets.

Figure 13.18 (page 508)



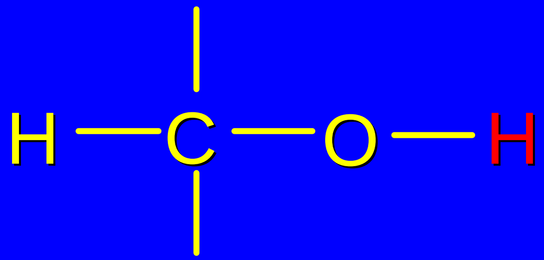
doublet doublet

doublet of doublets

13.12
^{1}H NMR Spectra of Alcohols

What about H bonded to O?

O—H



$H-C-O-H$

The chemical shift for O—H is variable (δ 0.5-5 ppm) and depends on temperature and concentration.

Splitting of the O—H proton is sometimes observed, but often is not. It usually appears as a broad peak.

Adding D_2O converts O—H to O—D. The O—H peak disappears.

13.13
NMR and Conformations

NMR is "slow"

Most conformational changes occur faster than NMR can detect them.

An NMR spectrum is the weighted average of the conformations.

For example: Cyclohexane gives a single peak for its H atoms in NMR. Half of the time a single proton is axial and half of the time it is equatorial. The observed chemical shift is half way between the axial chemical shift and the equatorial chemical shift.